● Phase space averages of dynamical variables

We showed in the last lecture that a dynamical variable, say $B$, evolves in time from some initial microstate $\Gamma(0) \equiv \Gamma$ according to the following Liouville-like equation

$$\frac{\partial B}{\partial t} = iLB , \tag{1a}$$

whose formal solution is

$$B(t) = e^{itL}B(0) \tag{1b}$$

where $B(t) = B(t;\Gamma)$ and $B(0) = B(\Gamma)$. With this solution in hand, we're in a position to construct the ensemble average of $B$, which by definition is

$$\langle B(t) \rangle = \int d\Gamma B(t;\Gamma) f(\Gamma) \tag{2}$$

Note that this expression is not the *equilibrium* ensemble average we introduced earlier; that average involved the *equilibrium* probability density function $P(\Gamma)$, which $f(\Gamma)$ can be equated to only when the system of interest is in fact in equilibrium. We'll explore this equilibrium limit soon. Using Eq. (1b) in Eq. (2), we see that

$$\langle B(t) \rangle = \int d\Gamma f(\Gamma) e^{iLt} B(\Gamma) \tag{3}$$

This is actually not the only way we could have defined the ensemble average of $B$ at time $t$. Instead of following $B$ as it evolves for a time $t$ along a trajectory determined by the phase point $\Gamma$, which at time 0 occurs with the weight $f(\Gamma)$, we could instead have located ourselves at $\Gamma$ (where $B$ has the value $B(\Gamma)$) and then tracked how the density distribution of $\Gamma$ itself changed over the course of the time interval $t$. In that scenario, we can define $\langle B(t) \rangle$ as

$$\langle B(t) \rangle = \int d\Gamma B(\Gamma) f(t;\Gamma)$$

$$= \int d\Gamma B(\Gamma) e^{-iLt} f(\Gamma) \tag{4}$$

If Eq. (4) is indeed an acceptable alternative definition of $\langle B(t)\rangle$, we should be able to show rigorously that Eqs. (3) and (4) are equivalent. We'll now demonstrate that we can in fact do this.

Proof

Start from Eq. (3), and introduce the series representation of the exponential operator:

$$\langle B(t)\rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \int d\Gamma f(\Gamma)(iLt)^n B(\Gamma)$$

$$= \sum_{n=0}^{\infty} \frac{1}{n!} \int d\Gamma f(\Gamma)(iLt)(iLt)^{n-1} B(\Gamma)$$

$$= \sum_{n=0}^{\infty} \frac{t^n}{n!} \int d\Gamma f(\Gamma)\left(\dot{\Gamma}\cdot\frac{\partial}{\partial\Gamma}\right)\left(\dot{\Gamma}\cdot\frac{\partial}{\partial\Gamma}\right)^{n-1} B(\Gamma) \tag{5}$$

The right hand side of Eq. (5) is a complex expression involving integrations and differentiations over all the components of $N$ positions and momenta, but if we ignore the multi-dimensional character of $\Gamma$ for the moment and take the view (which we'll have to justify later) that we can treat it as though it were just a *single* variable, we can carry out these operations fairly simply. So as a first step, let's integrate (5) by parts. The result is

$$\langle B(t)\rangle = \sum_{n=0}^{\infty} \frac{t^n}{n!}\left[ f(\Gamma)\dot{\Gamma}\left(\dot{\Gamma}\cdot\frac{\partial}{\partial\Gamma}\right)^{n-1} B(\Gamma)\Bigg|^S - \int d\Gamma\left\{\left(\dot{\Gamma}\cdot\frac{\partial}{\partial\Gamma}\right)^{n-1} B(\Gamma)\right\}\frac{\partial}{\partial\Gamma}\cdot\dot{\Gamma}f(\Gamma)\right] \tag{6}$$

The first term in the square brackets (the integrated term) must be evaluated at the upper and lower limits of the integration variables, which means evaluating it at $\{\mathbf{q}^N\}\to\infty$ and $\{\mathbf{p}^N\}\to\infty$. We can safely assume that there will be no microstates with infinite momenta, so $f(\Gamma)$ in this limit vanishes, and the surface term can therefore be discarded, leaving us with

$$\langle B(t)\rangle = -\sum_{n=0}^{\infty} \frac{t^n}{n!} \int d\Gamma\left[\left(\dot{\Gamma}\cdot\frac{\partial}{\partial\Gamma}\right)^{n-1} B(\Gamma)\right]\left(\frac{\partial}{\partial\Gamma}\cdot\dot{\Gamma}f(\Gamma)\right) \tag{7}$$

Again, viewing $\Gamma$ as a single variable, we can use the product rule to differentiate the last term in parentheses, obtaining:

$$\frac{\partial}{\partial\Gamma}\cdot\dot{\Gamma}f(\Gamma) = \dot{\Gamma}\cdot\frac{\partial f(\Gamma)}{\partial\Gamma} + f(\Gamma)\frac{\partial}{\partial\Gamma}\cdot\dot{\Gamma} \tag{8}$$

The last term in (8) also vanishes; this follows from the definition of $\Gamma$ and Hamilton's equations:

$$\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} = \sum_{i=1}^{N} \left( \frac{\partial}{\partial \mathbf{q}_i} \cdot \dot{\mathbf{q}}_i + \frac{\partial}{\partial \mathbf{p}_i} \cdot \mathbf{p}_i \right)$$

$$= \sum_{i=1}^{N} \sum_{\alpha} \left( \frac{\partial}{\partial q_{i\alpha}} \dot{q}_{i\alpha} + \frac{\partial}{\partial p_{i\alpha}} \dot{p}_{i\alpha} \right)$$

$$= \sum_{i=1}^{N} \sum_{\alpha} \left( \frac{\partial}{\partial q_{i\alpha}} \frac{\partial H}{\partial p_{i\alpha}} - \frac{\partial}{\partial p_{i\alpha}} \frac{\partial H}{\partial q_{i\alpha}} \right)$$

$$= 0 \tag{9}$$

Substituting this result into (7), we get

$$\langle B(t) \rangle = -\sum_{n=0}^{\infty} \frac{t^n}{n!} \int d\Gamma \left[ \left( \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \right)^{n-1} B(\Gamma) \right] \left( \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} f(\Gamma) \right) \tag{10}$$

We now repeat these steps, first writing Eq. (10) as

$$\langle B(t) \rangle = -\sum_{n=0}^{\infty} \frac{t^n}{n!} \int d\Gamma \left[ \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \left( \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \right)^{n-2} B(\Gamma) \right] \left( \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} f(\Gamma) \right)$$

then integrating by parts. After discarding the surface term, and using (8) and (9), we find that

$$\langle B(t) \rangle = \sum_{n=0}^{\infty} \frac{t^n}{n!} \int d\Gamma \left[ \left( \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \right)^{n-2} B(\Gamma) \right] \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \left( \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} f(\Gamma) \right)$$

$$= \sum_{n=0}^{\infty} \frac{t^n}{n!} \int d\Gamma \left[ \left( \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \right)^{n-2} B(\Gamma) \right] \left( \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \right)^2 f(\Gamma)$$

After carrying out these operations another $n - 2$ times, we're finally left with

$$\langle B(t) \rangle = \sum_{n=0}^{\infty} \frac{(-1)^n t^n}{n!} \int d\Gamma B(\Gamma) \left( \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} \right)^n f(\Gamma)$$

$$= \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int d\Gamma B(\Gamma) (iLt)^n f(\Gamma)$$

$$= \int d\Gamma B(\Gamma) e^{-iLt} f(\Gamma)$$

$$= \int d\Gamma B(\Gamma) f(t; \Gamma)$$

And so, in the end

$$\int d\Gamma f(\Gamma) B(t; \Gamma) = \int d\Gamma B(\Gamma) f(t; \Gamma) \tag{11}$$

● <u>Equilibrium Averages</u>

Recall that the probability density function of phase points, $f$, is governed by the Liouville equation, viz.:

$$\frac{\partial f}{\partial t} = -iLf \tag{12}$$

If it so happens that

$$\frac{\partial f}{\partial t} = 0 \tag{13}$$

we refer to the associated distribution function as the *equilibrium density distribution*, and denote it $f_0$. It is the time-independent probability density that a system under a given set of external constraints (such as constant $T$, $V$ and $N$) is in the microstate $\Gamma$, and it is the same as the quantity introduced earlier as $P(\Gamma)$. We've learnt what the functional forms of these distributions are from equilibrium statistical mechanics. They are recapitulated in the table below:

| Macrostate | $f_0(\Gamma) \equiv P(\Gamma)$ | Thermodynamic connection | Partition Function |
|---|---|---|---|
| $U, V, N$ | $\dfrac{1}{\Omega}$ | $S = k_B \ln \Omega$ | $\Omega = \dfrac{1}{h^{3N}N!}\int d\Gamma\, \delta(U - H_\Gamma))$ |
| $T, V, N$ | $\dfrac{1}{h^{3N}N!Q}e^{-\beta H_\Gamma}$ | $F = -k_B T \ln Q$ | $Q = \dfrac{1}{h^{3N}N!}\int d\Gamma\, e^{-\beta H_\Gamma}$ |
| $T, P, N$ | $\dfrac{1}{h^{3N}N!V_R \Delta}e^{-\beta(H_\Gamma + PV)}$ | $G = -k_B T \ln \Delta$ | $\Delta = \dfrac{1}{h^{3N}N!V_R}\int\limits_0^\infty dV \int d\Gamma\, e^{-\beta(H_\Gamma + PV)}$ |
| $T, V, \mu$ | $\dfrac{1}{h^{3N}N!\Xi}e^{-\beta(H_\Gamma - N\mu)}$ | $\Psi = -k_B T \ln \Xi$ | $\Xi = \sum\limits_{N=0}\dfrac{1}{h^{3N}N!}\int d\Gamma\, e^{-\beta(H_\Gamma - N\mu)}$ |

Some points to note:

● $\beta$ is an abbreviation for $1/k_B T$.

● $h$ stands for Planck's constant. Its appearance in the above formulas reflects the fact that phase space is not infinitely divisible, and cannot occupy a volume smaller than the scale set by $h$. The existence of this smallest volume is ultimately a consequence of Heisenberg's uncertainty principle, which places limits on the precision with which the position and momentum of a particle can be measured. The presence of factors of $h$ also ensures that the partition functions are properly dimensionless since $h$ has the units of a position times a momentum. (In the case of the isothermal-isobaric partition function, a reference volume $V_R$ is included to ensure that $\Delta$ is dimensionless. In the case of the microcanonical partition function, a similar reference energy, say, $U_R$, must be understood to multiply the right hand side, since the delta function has units of Energy$^{-1}$ [which is a consequence of the following property of the delta function: $\delta(ax) = \dfrac{1}{|a|}\delta(x)$.] Both $V_R$ and $U_R$ will drop out when calculating averages of physical quantities.)

● The factors of $N!$ in the various formulas account *approximately* for the indistinguishability of particles. In classical mechanics, it's possible, in principle, to distinguish particles by their positions and momenta, but at a fundamental quantum mechanical level, particles can't be so distinguished even in principle (again, because of the uncertainty principle.) The factors of $N!$ correct for this fundamental indistinguishability, but they only work for systems at high temperatures. If temperatures are sufficiently low that the thermal de Broglie wavelength of the particles is comparable

to their linear dimensions, this correction factor no longer works, and the particle must be treated quantum mechanically.

Some properties of the equilibrium density distribution

● Consider a system at constant $T$, $V$ and $N$, where $f_0(\Gamma)$ is given by

$$f_0(\Gamma) = Ce^{-\beta H(\Gamma)}$$

with $C$ standing for $1/h^{3N} N! Q$. Apply the Liouville operator to this function:

$$iLf_0 = \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} Ce^{-\beta H}$$

$$= -C\beta e^{-\beta H} \dot{\Gamma} \cdot \frac{\partial H}{\partial \Gamma}$$

$$= -C\beta e^{-\beta H} \sum_{i=1}^{N} \left( \dot{\mathbf{q}}_i \cdot \frac{\partial H}{\partial \mathbf{q}_i} + \dot{\mathbf{p}}_i \cdot \frac{\partial H}{\partial \mathbf{p}_i} \right)$$

Introducing Hamilton's equations into the above expression, we get

$$iLf_0 = -C\beta e^{-\beta H} \sum_{i=1}^{N} \left( \dot{\mathbf{q}}_i \cdot (-\dot{\mathbf{p}}_i) + \dot{\mathbf{p}}_i \cdot \dot{\mathbf{q}}_i \right)$$

$$= 0$$

This implies that

$$\frac{\partial f_0}{\partial t} = 0$$

So the canonical distribution is time-independent (as are the other density distributions in the table above) , just as equilibrium density distributions are expected to be. In other words

$$f_0(0) = f_0(t_1) = \cdots\cdots = f_0(t_n) = \cdots\cdots$$

● The use of equilibrium density distributions to construct an ensemble average of the dynamical variable $B$ has the immediate implication that $\langle B(t) \rangle$ is stationary, i.e., that $\langle B(t) \rangle$ is a constant, independent of time, or that $\partial \langle B(t) \rangle / \partial t = 0$. This result can be proved rigorously.

<u>Proof</u>

By definition

$$\left\langle B(t) \right\rangle = \int d\Gamma f_0(\Gamma) B(t;\Gamma)$$

$$= \int d\Gamma f_0(\Gamma) e^{itL} B(\Gamma)$$

Differentiating this expression with respect to $t$, we get

$$\frac{\partial \left\langle B(t) \right\rangle}{\partial t} = \int d\Gamma f_0(\Gamma) iL e^{itL} B(\Gamma)$$

$$= \int d\Gamma f_0(\Gamma) \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} e^{itL} B(\Gamma)$$

Partial integration and elimination of the surface terms leads to

$$\frac{\partial \left\langle B(t) \right\rangle}{\partial t} = -\int d\Gamma \left[ e^{itL} B(\Gamma) \right] \dot{\Gamma} \cdot \frac{\partial}{\partial \Gamma} f_0(\Gamma) \quad (\text{because } \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} = 0 )$$

$$= -\int d\Gamma \left[ e^{itL} B(\Gamma) \right] iL f_0(\Gamma)$$

$$= 0$$

So $\left\langle B(t) \right\rangle$ is indeed stationary, as we'd argued earlier it should be on purely physical grounds. Now we have a more rigorous basis for this property.

This result follows more simply from the definition $\langle B(t) \rangle = \int d\Gamma B(\Gamma) f(t;\Gamma)$, which for the special case of an equilibrium distribution, reduces to $\langle B(t) \rangle = \int d\Gamma B(\Gamma) f_0(\Gamma)$. The right hand side of this relation is clearly independent of time, and so $\frac{\partial \langle B(t) \rangle}{\partial t} = 0$.